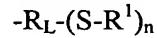


CLAIMS

WHAT IS CLAIMED IS:

1. A polyurethane comprising a thiol substituent pendant from at least one nitrogen and/or at least one carbon atom of the polyurethane.

5 2. The polyurethane of claim 1, wherein the thiol substituent has a formula:



wherein n is an integer from 1 to 3;  $R_L$  is an  $(n+1)$ -valent organic radical comprising at least one carbon atom; and  $R^1$  is a member selected from the group consisting of H,  $C(O)R^3$ , and  $SR^4$ , 10 wherein  $R^3$  is a member selected from the group consisting of  $C_1$  to  $C_6$  alkyl and  $R^4$  is a heterocyclic group or an electron deficient aromatic group.

15 3. The polyurethane of claim 2, wherein  $R_L$  is a bivalent organic radical selected from the group consisting of  $C_1$  to  $C_{18}$  alkylene,  $C_1$  to  $C_{18}$  alkyleneamino,  $C_1$  to  $C_{18}$  alkyleneoxy,  $C_1$  to  $C_{18}$  haloalkylene,  $C_2$  to  $C_{18}$  alkenylene,  $C_6$  to  $C_{18}$  arylene, a modified  $C_2$  to  $C_{18}$  alkenylene having at least one carbon substituted by a halogen group,  $C_2$  to  $C_{18}$  alkenylene having one or more O, S, or N atoms incorporated into an alkenylene chain, a bivalent heterocyclic radical, and mixtures thereof.

20 4. The polyurethane of claim 3, wherein  $R_L$  is  $C_1$  to  $C_6$  alkylene.

5. The polyurethane of claim 4, wherein  $R_L$  is butylene.

25 6. The polyurethane of claim 3, wherein the bivalent heterocyclic radical is a member selected from the group consisting of thiazoline, thiazolidone, imidazole, imidazoline, thiazole, tetrazole, thiadiazole, imidazole, pyridine, and morpholine.

7. The polyurethane of claim 6, wherein the bivalent heterocyclic radical is pyridine.

8. The polyurethane of claim 2, wherein  $R^1$  is H.

25 9. The polyurethane of claim 2, wherein  $R^1$  is  $SR^4$ .

10. The polyurethane of claim 2, wherein  $R^4$  is 2-pyridyl.

11. The polyurethane of claim 2, wherein  $R^4$  is 3-carboxy-4-nitrophenyl.

12. The polyurethane of claim 1, wherein the thiol substituent is pendant from about 0.5 to 50% of urethane nitrogen atoms.

30 13. The polyurethane of claim 1, wherein the thiol substituent is pendant from about 0.5 to about 50% of carbon atoms.

14. The polyurethane of claim 1, wherein the thiol substituent is pendant from 1 to 20% of urethane nitrogen and/or carbon atoms.

15. The polyurethane of claim 1, wherein the thiol substituent is pendant from 5 to 10% of urethane nitrogen and/or carbon atoms.

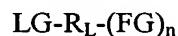
16. The polyurethane of claim 1, wherein the polyurethane comprises at least about 10 micromoles of the thiol substituent per gram of the polyurethane.

5 17. The polyurethane of claim 1, wherein the polyurethane has at least two different thiol substituents pendant from urethane nitrogen and/or carbon atoms.

18. The polyurethane of claim 1, wherein the thiol substituent is an acetylthio group.

19. The polyurethane of claim 1, wherein the thiol substituent is a 3-carboxy-4-nitrophenyldithio group.

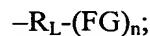
10 20. A process for preparing the polyurethane of claim 1, the process comprising: providing a polyurethane comprising a urethane amino moiety; providing a multifunctional linker reagent of a formula:



15 wherein n is an integer from 1 to 3, FG is a functional group selected from the group consisting of a halogen, a carboxyl group, a sulfonate ester, and an epoxy group, LG is a leaving group selected from the group consisting of a halogen, a carboxyl group, a sulfonate ester, and an epoxy group, and R<sub>L</sub> is an (n+1)-valent organic radical comprising at least one carbon atom;

20 providing a protected thiol-containing reagent of a formula R-C(O)SH, or a salt thereof, wherein R is a C<sub>1</sub> to C<sub>6</sub> alkyl group;

reacting the multifunctional linker reagent with the urethane amino moiety to form a polyurethane substituted with at least one substituent group of a formula



25 reacting the polyurethane substituted with at least one substituent group with a protected thiol-containing reagent to form the polyurethane comprising the thiol substituent pendant from the at least one nitrogen and/or the at least one carbon atom.

21. The process of claim 20, wherein R<sub>L</sub> is a bivalent organic radical selected from the group consisting of C<sub>1</sub> to C<sub>18</sub> alkylene, C<sub>1</sub> to C<sub>18</sub> alkyleneamino, C<sub>1</sub> to C<sub>18</sub> alkyleneoxy, C<sub>1</sub> to C<sub>18</sub> haloalkylene, C<sub>2</sub> to C<sub>18</sub> alkenylene, C<sub>6</sub> to C<sub>18</sub> arylene, a modified C<sub>2</sub> to C<sub>18</sub> alkenylene having at least one carbon substituted by a halogen group, C<sub>2</sub> to C<sub>18</sub> alkenylene having one or 30 more O, S, or N atoms incorporated into an alkenylene chain, a bivalent heterocyclic radical, and mixtures thereof.

22. The process of claim 21, wherein R<sub>L</sub> is a member selected from the group consisting of C<sub>1</sub> to C<sub>6</sub> alkylene.

23. The process of claim 21, wherein R<sub>L</sub> is butylene, FG is a bromo group, LG is a bromo group and n is 1.

24. The process of claim 20, wherein LG is a bromo group.

25. The process of claim 20, wherein the sulfonate ester is a member selected from the group consisting of mesylate, triflate, and tosylate.

26. The process of claim 20, wherein the sulfonate ester is a member selected from the group consisting of a  $\omega$ -bromoalkyl mesylate, a  $\omega$ -bromoalkyl triflate, and a  $\omega$ -bromoalkyl tosylate.

27. The process of claim 20, wherein the multifunctional linker reagent is a member selected from the group consisting of a dibromoalkyl compound, a bromo-carboxyalkyl compound, and a bromo-epoxyalkyl compound.

28. The process of claim 27, wherein the dibromoalkyl compound is a 1, $\omega$ -dibromoalkyl compound or a substituted 1,  $\omega$ -dibromoalkyl compound.

29. The process of claim 28, wherein the dibromoalkyl compound is a C<sub>2</sub>-C<sub>6</sub>1, $\omega$ -dibromoalkyl compound.

30. The process of claim 28, wherein the dibromoalkyl compound is 1,6-dibromohexane or 1,4-dibromobutane.

31. The process of claim 27, wherein the bromo-carboxyalkyl compound is a  $\omega$  -bromocarboxylic acid or a substituted  $\omega$  -bromocarboxylic acid.

32. The process of claim 27, wherein the bromo-epoxyalkyl compound is epibromohydrin.

33. The process of claim 20, wherein the process is conducted in a presence of an aprotic solvent.

34. The process of claim 33, wherein the aprotic solvent is a member selected from the group consisting of N,N-dimethylacetamide, N,N-dimethyl formamide, 1-methyl-2-pyrrolidinone, tetrahydrofuran, dioxane, and dimethyl sulfoxide.

35. The process of claim 20, wherein the process is conducted in a presence of a base soluble in the aprotic solvent.

36. The process of claim 35, wherein the base is a member selected from the group consisting of sodium hydride, lithium diisopropylamide, and sodium.

37. The process of claim 35, wherein the base is potassium tert-butoxide, dimsyl sodium, lithium hydride, sodium amide, lithium N,N-dialkylamide, or lithium N,N-dicyclohexylamide.

38. The process of claim 35, wherein the base is lithium tert-butoxide.
39. The process of claim 37, wherein the multifunctional linker reagent is 1,6-dibromohexane, and the base is lithium diisopropylamide.
40. The process of claim 28, wherein the multifunctional linker reagent is 1,4-dibromobutane.
- 5 41. The process of claim 20, wherein the protected thiol-containing reagent is thiolacetic acid.
42. The process of claim 20, wherein the protected thiol-containing reagent is tetrabutylammonium thioacetate.
- 10 43. The process of claim 20, further comprising reacting the protected thiol group with a deprotecting reagent to remove an R-C(O)- fragment from the thiol substituent to obtain the polyurethane.
- 15 44. The process of claim 43, wherein the deprotecting reagent is a member selected from the group consisting of ammonia, primary aliphatic amines, aqueous solutions of alkali metal hydroxides, carbonates, tri-substituted phosphates, hydroxylamine, and hydrazine.
45. A process of producing a molded product, said process comprising:  
providing the polyurethane of claim 1, wherein the thiol substituent is protected;  
molding the polyurethane to form an article; and  
deprotecting the thiol substituent of the article to provide the molded product.
- 20 46. The process of claim 45, further comprising reacting the thiol substituent of the molded product with a biomolecule.
47. A molded product produced by the process of claim 45.
48. The molded product of claim 47, wherein the molded product is an implantable device.